

Emission of dimethylsulfide from Weddell Sea leads

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[1] The distribution of dimethylsulfide (DMS), dimethylsulfoniopropionate (DMSP) and dimethylsulfoxide (DMSO) was examined in lead water in pack ice of the Weddell Sea. Samples were taken by pulling water into a syringe from a series of depths from 0.002 m to 4 m and deeper. Concentrations of DMS, DMSP and DMSO remained low throughout the water column relative to surface water, which was highly enriched. Concentrations of the major sulfur compounds increased by over an order of magnitude during periods with smooth surface water conditions. This increase coincided with a profound stratification of the water column, caused by a decrease in salinity of near surface water. We estimate that the DMS emission from leads and open water in Antarctic sea ice could contribute significantly to the yearly DMS flux from the Southern Ocean.

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1. Introduction

[2] Dimethylsulfide and related compounds, dimethylsulfoniopropionate (DMSP) and dimethylsulfoxide are increasingly being used as models for biogeochemical cycling of trace gases. Many global climatological maps of sea surface dimethylsulfide have been constructed by, e.g., *Belviso et al.* [2004, and references therein]. This approach forms the basis for estimates of contemporary DMS air-sea fluxes [e.g., *Kettle and Andreae*, 2000]. However, the uncertainty between the different DMS climatologies ranges from 50% in tropical to nearly 100% in high latitudinal regions. Moreover, high latitudinal ice covered oceanic zones are not taken into account in the current climatologies.

[3] Sea ice formation is an important characteristic of both polar regions which at its maximum extent covers 6% of the Earth's surface [*Gloersen et al.*, 1992]. In the Southern Ocean the annual extent of sea ice ranges from a minimum of 4×10^6 km² to a maximum of 19×10^6 km², and forms one of the largest biomes on Earth. Sea ice research over the past decades has improved our understanding of many of the physical processes that transform surface waters into a matrix of ice and liquid, and the role this has on large scale processes, such as ocean

circulation and air-ocean exchange. Beneath the snow and between floes lie unique habitats that appear to be highly productive during spring and summer and are thought to make a major contribution to global sulfur and carbon cycling [*Trevena et al.*, 2003; *Semiletov et al.*, 2004].

[4] Here we present data from a study of the vertical distribution of sulfur compounds in near-surface water between floes of the multi year ice zone of the western Weddell Sea. The data show a sharp drop in salinity towards the surface, concurrent with a significant increase of DMS, DMSP and DMSO. Assuming an average fraction of open water of 5% (based on aerial photographs over the study region), DMS emission from lead water in December could be 0.4% of the yearly DMS flux from the Southern Ocean.

2. Sampling

[5] The study was performed during the 2004 Ice Station Polarstern (ISPOL) cruise, a field experiment designed to improve understanding of physical and biological air-sea-ice interactions in the Weddell Sea through early summer. ISPOL involved a 37 day drift station on an ice floe (from 68°15'S, 54°45'W to 67°22'S, 55°25'W) in the western Weddell Sea. Water temperature and wind speed were derived from the ship's meteorological system. Sea ice conditions were monitored from helicopters using aerial photography to determine snow coverage, ice thickness and concentration. Sea water was sampled from two leads. Lead 1 was newly opened and was sampled from day 350 through 359. Lead 2 was two weeks old when sampling started from day 362 through day 001. Sampling the two leads occurred between 12:00 and 16:00 GMT and started after a period of elevated wind speeds during which waves mixed the upper water column. Samples in lead 1 were taken at 0.002 m, 0.25 m, 1 m, and 4 m. Lead 2 was also sampled at 0.1 m depth. Samples were taken by suspending 0.001 m (internal diameter) Teflon sampling inlets from a small catamaran and by pulling water into a 50 ml syringe at a speed of 5 ml min⁻¹. Sample collection at different withdrawal speeds (2 ml min⁻¹, 5 ml min⁻¹, and 50 ml min⁻¹) and with different syringes (glass and plastic) showed no significant effect on the concentration of sulfur compounds ($n = 20$, $p < 0.05$).

[6] Inlets and syringes were rinsed three times before water was collected into 50 ml glass reaction vials for analysis of sulfur compounds, followed by collection of 150 ml for salinity analysis. In total 0.5 L water was taken from water close to the surface and 1 L from 1 and 4 m depth. In addition water from below the ice was sampled through a hole drilled through the ice (thickness 2 m) with sample inlets at six half meter intervals between the bottom of the ice and 2.5 m below the ice. Water samples were also collected through the ship's seawater inlet at 11 m depth. Samples were brought back to the (ship's) laboratory for

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Table 1. Yearday, Wind Speed (m s^{-1}), DMSP_t, DMS and DMSO_t Concentration (nM) at 0.002 m and 0.25 m, and Average Flux (gS d^{-1}) Over a Lead Area of $6.5 \times 10^4 \text{ km}^2$, Which Corresponds to 5% Open Water in the Multi Year Ice Zone of the Western Weddell Sea in December^a

Yearday	Windspeed, m s^{-1}	DMSP _t (nM) Depth, m		DMS(aq)(nM) Depth, m		Flux, gS d^{-1}	DMSO _t (nM) Depth, m	
		0.002	0.25	0.002	0.25		0.002	0.25
350	4.08	12	6	0.8	0.7	3.3E+05	-	-
352	3.68	10	4	1.1	0.9	2.0E+05	8	6
354	8.43	55	8	4.7	0.6	1.6E+07	17	12
356	3.97	78	18	7.8	1.5	3.0E+06	18	4
358	5.54	84	10	9.7	1.0	1.4E+07	38	10
359	5.08	81	14	18.6	5.3	2.1E+07	95	18
362	9.2	18	13	2.9	0.9	1.1E+07	11	5
363	7.85	27	16	3	0.7	8.8E+06	13	5
364	5.38	25	15	18.7	0.7	2.5E+07	16	2
365	4.43	98	13	44	1.9	3.1E+07	116	7
367	4.72	84	12	45.9	1.8	4.1E+07	191	7

^aThe flux is calculated using the *Liss and Merlivat* [1986] parameterization for gas exchange.

immediate analysis (of DMS), or treated for overnight hydrolysis and next day analysis (total DMSP), or stored for later analysis (total DMSO) usually within 72 h [see also *Zemmelink et al.*, 2005]. Storage occurred between 0–5°C in the dark. DMS, DMSP and DMSO concentrations were determined using a purge and trap gas chromatography procedure. All samples and standards were analyzed in triplicate with an analytical precision of 98% for DMS at the 1–2 nM range, 95% for DMSP in the 4–6 nM, and 90% for DMSO in the 5–10 nM range. Surface and deep water samples were taken in order to test the effect of filtration on DMS concentrations. Subsamples of 2–4 ml were collected under gravity filtration over Whatman GF-C. Results indicated that there was no difference between unfiltered and filtered water collected at the start of the experiment from the surface (18.6 ± 0.3 ; 18.6 ± 0.4 , respectively), from 4 m depth (5.3 ± 0.2 ; 5.3 ± 0.4 , respectively); nor in surface water (unfiltered: 44.3 ± 0.9 ; filtered: 44.1 ± 0.7), or deep water (unfiltered: 1.9 ± 0.1 ; filtered: 1.9 ± 0.1) collected at the end of the experiment. (Numbers between parenthesis refer to the average ($n = 6$) \pm standard deviation). Salinity was analyzed using a Guildline Autosol 8400B laboratory salinometer, error $< \pm 0.002$ equivalent ‰.

3. Results

[7] Water temperature was about -1.8°C and wind speed varied between 3.6 and 9.2 m s^{-1} (Table 1). The relative position of the sample site to the direction of the wind varied from down wind to up wind. Aerial photography data revealed a number of significant changes in the character of the pack ice between 29 November 2004 and 1 January 2005. There was a net decrease in the concentration of thick, snow-covered floes from 96% to 90%, however this did not reflect a net decrease in total ice concentration. Instead we observed an increase from 1% to 7% in the amount of brash ice between the floes, much of which was brown due to the high diatom concentrations, and therefore highly productive. This coincided with a net decrease in floe size, while the open water fraction averaged 5% throughout December. Also clearly visible in the aerial photographs are large areas of surface flooding that developed towards the end of the experiment. These extended tens to hundreds of meters

across some floes and would result in increased run off of snow melt into leads. The largest changes in sea ice characteristics were observed towards the end of December.

[8] Data obtained from the two leads are presented in Table 1 and Figure 1, where plots A, C, E, and G refer to lead 1, and plots B, D, F, and H refer to lead 2. The maximum width of lead 1 varied between 1 m and 50 m due to relative motion of adjacent floes, the width at the first sampling day was about 5 m. The width of lead 2 remained constant throughout the study and was about 10 m. During both studies the water column appeared to be well mixed at the first sampling day, which was caused by the elevated wind speed and short breaking waves during the preceding days. No profiles were observed during such conditions but stratification rapidly occurred, and enhanced with time, when breaking waves were not present. Salinity at the sea surface dropped from 34 to 28.6‰ during the first period (Figure 1a) and even more during the second, when salinity dropped to 27.4‰ (Figure 1b). Water below 0.1 m remained at salinity around 34.3‰ throughout the measurement period.

[9] In lead 1 DMSP concentrations varied from 4 to 14 nM at 0.25 m, with the exception of day 356 when DMSP concentrations at 0.1, 2 and 4 m depth were around 18 nM. At the surface DMSP varied from 9 to 85 nM with higher values towards day 359 (Figure 1c). DMSP in lead 2 varied from 12 to 16 nM at 0.25 m depth and surface DMSP increased to values close to 100 nM towards the end of December (Figure 1d). Samples collected beneath the ice and at 11 m (data not shown) showed DMSP concentrations that corresponded to concentrations found at 2.5 and 4 m depth.

[10] Similar to DMSP, DMS shows higher concentrations towards the sea surface. While early December values between 0.25 m depth and deeper (not shown) averaged about 0.6 nM, surface values increased to 4.7 nM. Values by day 359 had increased to 18.6 nM (Figure 1e). Concentrations at 0.25 m depth in lead 2 were similar to values found in lead 1 and varied around 1.2 nM, increasing to surface values of 46 nM by early January (Figure 1f).

[11] At the surface DMS is subject to outgassing to the atmosphere and photochemical oxidation to DMSO, the latter making linearity of DMS gradients towards

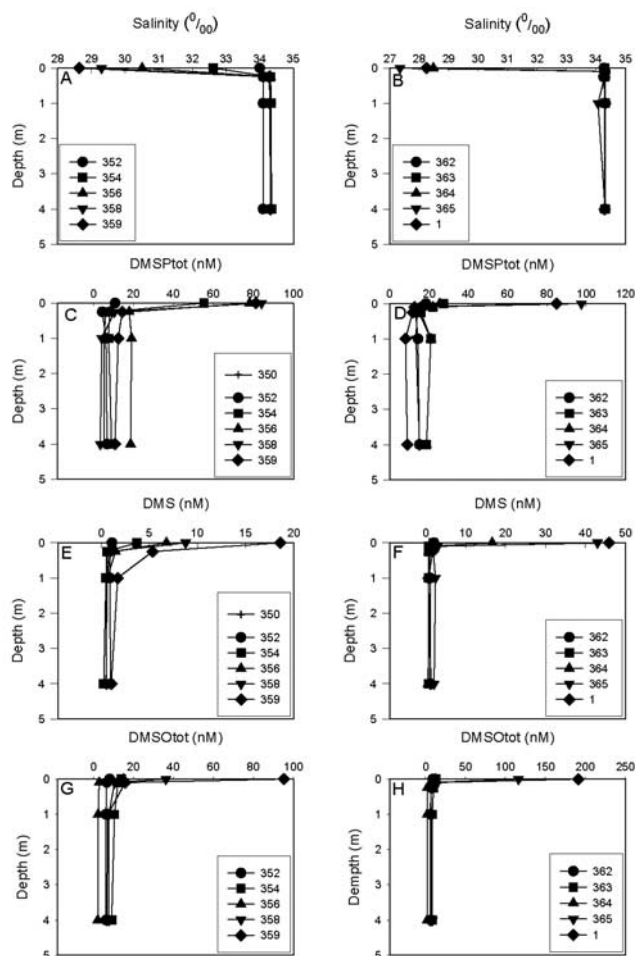


Figure 1. Salinity (‰), DMSP_t, DMS and DMSO_t (nM) from 0.002 m to 4 m depth in the water column of two Antarctic leads. Plots A, C, E, G refer to lead 1, and plots B, D, F, H refer to lead 2. Time series are from 10-Dec-04 (day 350) to 24-Dec-04 (day 359) and from 27-Dec-04 (day 362) to 01-Jan-05 (day 01).

the boundary layer between the water and overlying air unlikely. In addition to photo-oxidation, DMSO is also likely to be produced via a biosynthetic pathway [e.g., Besiktepe *et al.*, 2004]. DMSO concentrations showed, as with DMS and DMSP, an increase towards the water surface (Figures 1g and 1h). Concentrations at 0.25 m and deeper ranged from 2–18 nM while DMSO increased towards the sea surface to 8–13 nM in mixed conditions to 95 nM at day 359 and 191 nM at day 001.

4. Discussion

[12] Salinity data show that water obtained from 0.1 m and deeper is not representative of water near the surface, at least during calm sea surface conditions. Moreover, gradients of major sulfur compounds increased dramatically towards the surface and will probably change further towards the so called microlayer at the top of the water column. However, collection of 0.5 L water implies that a sample integrates a sphere of water with a diameter of about 5 cm. Therefore, the current study does not allow a more

precise determination of the depth of the pycnocline and of gradients towards the very surface.

[13] The fresh water above the pycnocline forms a habitat that is dominated by strong gradients in salinity and light. It is likely that this habitat favors some physiological and metabolic adaptations of organisms that thrive in this water layer. The accumulation of sulfur compounds might be from enhanced in situ production triggered by unique biological, chemical and physical characteristics in this part of the water column. E.g. close to the surface, in less saline water, DMSP might be released by algal cells that use this compound for osmotic protection. In addition photo-effects become important when stratification traps some part of the plankton community near the surface which could result in an enhanced accumulation of DMSP in algal cells (as part of a cellular anti-oxidant system [Sunda *et al.*, 2002]), enhanced lyses of DMSP to DMS, and an increased formation of DMSO via photochemical oxidation of DMS [Brimblecombe and Shooter, 1986]. However, the observed accumulation of sulfur compounds is not solely a result of in situ production but also originates from melting ice from adjacent floes, known to contain high concentrations of DMSP [Trevena *et al.*, 2003].

[14] The observed gradients are an important finding for sulfur dynamics, i.e. calculation of fluxes to the atmosphere (and to deeper water). Using the Liss and Merlivat [1986] parameterization for gas exchange and the measured water temperature, salinity, wind speed, and surface DMS values (Table 1), the flux of DMS from the leads can be estimated to vary between 0.1 and 20 $\mu\text{moles m}^{-2} \text{d}^{-1}$ (calculation of fluxes from the air-water concentration disequilibrium is extensively discussed in the literature e.g. Zemmeling *et al.* [2004]).

[15] The multi year ice zone in the western Weddell Sea extends to about $1.3 \times 10^6 \text{ km}^2$. Based on our knowledge from aerial photography that approximately 5% of this surface consists of leads ($6.5 \times 10^4 \text{ km}^2$) and assuming that our measured surface concentrations and wind speeds are representative for average values during December, the total sulfur flux during this month is 0.47 Gg. This is 0.04–0.4 % of the yearly flux over the Southern Ocean between 70°–60°S as calculated by Kettle and Andreae [2000]. The uncertainty is caused by the difference between data sets of sea surface DMS concentrations and wind speed used by Kettle and Andreae [2000]; their estimate of the sulfur flux ranges from 1.193 to 0.122 Tg y^{-1} . In addition, the open water area in the entire Weddell Sea region will continue to grow through January and February as the sea ice extent decreases from $4.3 \times 10^6 \text{ km}^2$ in December to its minimum of $1.3 \times 10^6 \text{ km}^2$ in February [Gloersen *et al.*, 1992]. With an increase in biological activity at the ice margin as summer progresses, this suggests that the emission of DMS from the entire Weddell Sea could be a significant contribution to the total sulfur flux from the Southern Ocean as estimated by Kettle and Andreae [2000].

[16] Our calculation is a very rough estimate of the DMS flux as it relies on assumptions that are based on a limited data set that does not provide enough insight in temporal and spatial variability of DMS in the surface ocean over longer time scales, where for instance biological productivity will continue to increase over summer. In addition, lead surface area varies day-to-day by refreezing

and with the cyclical periods of divergence and convergence caused by wind. The complex interaction between lead width and wind fetch eventually determines the emission of DMS. The character of the water surface of leads is extremely heterogeneous, with increasing turbulence and accumulation of brash ice towards the down wind site of the lead. The heterogeneity will also be apparent in the distribution of DMS and other compounds of interest. A straightforward calculation of the flux from surface values of DMS that are extrapolated over the whole surface area of leads (as in this study) will therefore be inaccurate. A more detailed study of surface characteristics (turbulence and sulfur compounds) and wind speed in leads is needed to gain more confidence in calculated fluxes.

[17] In conclusion, the results presented here demonstrate that in the absence of breaking waves large vertical gradients of chemical characteristics develop towards the surface of Antarctic lead water. The magnitude of the observed enrichments of sulfur compounds in the sea-surface result in significant fluxes towards the overlying atmosphere. Studies of sulfur cycling, usually based on samples taken from depths of up to several meters in open water, should take this pronounced gradient into consideration.

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